

## 4 Solubility Parameters

In the previous chapter, the types of interactions which can occur between solvent, cosolvent, and polymer molecules were described. The selection of a “good” solvent, which we will assume will be a solvent/cosolvent mixture, for a given polymer requires some method of quantifying the type and magnitude of each of these intermolecular interactions, both within each pure component and between components. If the type and strength of the interactions occurring within the solvent and polymer can be matched, then the thermodynamic conditions are tuned to provide favorable (attractive) interactions between them. The most widely used method for quantifying intermolecular interactions in condensed (liquid and solid) systems is the solubility parameter. The solubility parameter is obtained from an approximation of a system’s cohesive energy density, which, in turn, is intimately connected to the thermodynamic concept of internal pressure.

### 4.1 Cohesive Energy Density and Internal Pressure

The foundation of the first solubility parameter theory was developed as early as 1916<sup>204</sup> and was formalized by Hildebrand and Scott in 1950.<sup>205</sup> This theory was derived from an approximation of the internal pressure of a fluid, which was later termed the cohesive energy density, based on work conducted in 1928,<sup>206</sup> 1929,<sup>207</sup> 1932,<sup>208</sup> and 1950<sup>209</sup> where the two terms, internal pressure and cohesive energy density, were in fact

found to be nearly equivalent for nonpolar liquids. Subsequently, because of the ease in calculating the cohesive energy density of liquids at normal conditions, later workers have followed this approximation, so that the distinction between internal pressure and cohesive energy density has become blurred. This Section will examine the basis of internal pressure and the derivation of cohesive energy density in order to understand the significance of the two quantities, and their differences.

The first law of thermodynamics for a system that undergoes a change of state is

$$U_2 - U_1 = \Delta U = {}_1Q_2 - {}_1W_2 \quad (4-1)$$

where  $U_1$  and  $U_2$  are the initial and final values of the total energy  $U$  of the system,  ${}_1Q_2$  is the heat transferred to the system during the change from state 1 to 2, and  ${}_1W_2$  is the work done by the system during the change. In differential form, eqn. (4-1) is written as follows,

$$dU = \delta Q - \delta W \quad (4-2)$$

The physical significance of the property  $U$  is that it represents *all* the energy of the system in the given state. This energy might be present in a variety of forms, including the kinetic or potential energy of the system as a whole with respect to the chosen coordinate frame, energy associated with motion and position of the molecules, energy associated with structure of the atom, chemical energy such as is present in a storage battery, energy present in a charged condenser, etc.<sup>210</sup>

It is convenient to separate the kinetic energy (KE) and potential energy (PE) of the system as a whole, and then to consider all the remaining energy of the system in a single property called the internal energy,  $E$ . Therefore,

$$E + KE + PE = U \quad (4-3)$$

The first law for a change of state of a system may therefore be written as

$$dE + d(KE) + d(PE) = \delta Q - \delta W \quad (4-4)$$

If we assume that there are no changes in kinetic or potential energy of the system as a whole and that the only work done by the system during the process is the work of expansion by the system against its surroundings, then

$$dE = \delta Q - PdV \quad (4-5)$$

where  $PdV = \delta W$ . At this point we may define another property called entropy, designated by  $S$ . Entropy is defined as a property of a substance in accordance with the relation<sup>211</sup>

$$dS = \left( \frac{\delta Q}{T} \right)_{rev} \quad (4-6)$$

so that

$$\delta Q = TdS \quad (4-7)$$

for a reversible process. This leads to the following important thermodynamic relation for a simple compressible substance,

$$dE = TdS - PdV \quad (4-8)$$

Differentiating eqn. (4-8) with respect to  $V$  at constant  $T$

$$\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \left( \frac{\partial V}{\partial V} \right)_T \quad (4-9)$$

and using the Maxwell relation,

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (4-10)$$

gives “the thermodynamic equation of state”

$$\boxed{\left( \frac{\partial E}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P} \quad (4-11)$$

The individual terms in eqn. (4-11) can be defined as,

$$\left( \frac{\partial E}{\partial V} \right)_T = \text{Internal Pressure,}$$

$$T \left( \frac{\partial P}{\partial T} \right)_V = \text{Thermal Pressure,} \quad (4-12)$$

$P$  = External Pressure.

Equation (4-11) forms the basis of the cohesive energy density, developed by Hildebrand and Scott.<sup>212</sup> A brief outline of this work is as follows.

In general, a functional relationship among any three-system properties, for a one-component system, could be called an equation of state. However, by common usage the expression equation of state usually refers to relationships between pressure, temperature and specific volume.<sup>213</sup> Three broad classifications of equations of state can be identified, namely, generalized, empirical, and theoretical. The best known of the generalized equation of state is also the oldest, the van der Waals equation, which was presented in 1873 as a semi-theoretical improvement over the ideal gas equation.<sup>214</sup> The van der Waals equation of state is,

$$P + \frac{a}{V^2} = \frac{RT}{V - b} \quad (4-13)$$

where  $a$ ,  $b$  are called the attraction and repulsion parameter, respectively and are usually assumed to be constant for a given substance.<sup>215</sup> Differentiating the van der Waals equation with respect to  $T$  and constant  $V$

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{R}{V - b} \quad (4-14)$$

Substituting the result of eqn. (4-14) into eqn. (4-13) and comparing to eqn. (4-11) implies that

$$\left( \frac{\partial E}{\partial V} \right)_T = \frac{a}{V^2} \quad (4-15)$$

Scott went on to state that “over a small range of volumes”,  $E$  could be represented in the functional form,<sup>216</sup>

$$E = -\frac{a}{V^n} \quad (4-16)$$

so that by differentiating eqn. (4-16) with respect to volume at constant temperature,  $(\partial E/\partial V)_T$  can be expressed as<sup>217</sup>

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{na}{V^{n+1}} = \frac{-nE}{V} \quad (4-17)$$

Further, Scott states that for most practical purposes the cohesive energy per mole  $E$  may be replaced by  $-\Delta E$ <sup>218</sup> so that eqn. (4-17) can be rewritten as

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = \frac{n\Delta E}{V}} \quad (4-18)$$

Thus  $(\Delta E/V)$ , referred to by Hildebrand as the cohesive energy density, and  $(\partial E/\partial V)_T$ , the internal pressure, are related by the quantity  $n$ . It can be shown that for a liquid obeying van der Waals equation of state, eqn. (4-13),  $n = 1$ , and the cohesive energy density is therefore equal to the internal pressure. Further, Hildebrand and coworkers found that for nonpolar/nonassociating liquids, where intermolecular interactions are weak,  $n$  is, in fact, not far from unity.<sup>219,220,221</sup> Whereas for polar or associating liquids or liquids which are not greatly expanded over their close-packed structure, where repulsive forces play an important role (such as mercury at room temperature), the internal pressure is not equivalent to the cohesive energy density.

Table 4-1 gives a comparison of cohesive energy density and internal pressure for the solids and liquids, as evaluated by Hildebrand and Scott.

**Table 4-1.** Values of  $n$  for pure organic and inorganic liquids.<sup>222</sup>

Liquid	$\frac{m}{(D)^{223}}$ dipole moment	$V^2 \left( \frac{\partial E}{\partial V} \right)_T$ (kcal liters)	$V \Delta E^V$ (kcal liters)	$n$
n-Heptane	0.0	13.14	12.01	1.09
Silicon tetrachloride	0.0	8.23	7.56	1.09
Carbon tetrachloride	0.0	7.56	7.04	1.07
Benzene	0.0	7.07	6.70	1.05
Silicon tetrabromide	0.0	12.90	12.40	1.04
Stannic chloride	0.0	10.95	10.55	1.04
Titanium tetrachloride	0.0	10.15	9.98	1.02
Chloroform	1.1	5.76	5.67	1.02
Ethyl ether	1.3	6.58	6.49	1.01
Acetone	2.9	4.33	4.86	0.89
Carbon disulfide	0.0	3.27	3.67	0.89
Methanol	1.7	1.16	3.46	0.34
Mercury	-	0.69	2.11	0.33

In regards to the low value of  $n$  found for carbon disulfide Hildebrand<sup>224</sup> stated that while carbon disulfide has practically no dipole moment it is less symmetrical than carbon tetrachloride and it is therefore reasonable to expect a value less than unity. However in a similar experiment conducted in 1976,<sup>225</sup> a much different value for  $n$  was found for carbon disulfide (1.06) and it was suggested in this article that the earlier value was incorrect.

Since this early work of Hildebrand and others was conducted (spanning from 1928 to 1950), other studies<sup>226,227,228,229,230</sup> have evaluated the internal pressure and cohesive energy density for a range of liquid solvents. An expanded tabulation of  $(\partial E / \partial V)_T$  and  $(\Delta E / V)$ , along with the corresponding value of  $n$ , is given in Table 4-2

**Table 4-2.** Reported values of internal pressure, cohesive energy density, and  $n$  for pure liquids (sorted by decreasing values of  $n$ ).

Solvent	$\left(\frac{\partial E}{\partial V}\right)_T$ (J/cm <sup>3</sup> )	$\left(\frac{\Delta E}{V}\right)$ (J/cm <sup>3</sup> )	<b>m</b> (D) dipole moment	<b>n</b>	Ref
1,4-dioxane	493.7	396.2	0.45	1.2	231
Cyclohexane	321.8	282.3	0	1.14	232
Methylcyclohexane	296.7	260.2	0	1.14	233
Benzene	368.2	350.6	0	1.1	231
Carbon tetrachloride	338.9	307.9	0	1.1	231
Octane	266.1	242.3	0	1.1	233
Nonane	276.1	249.0	0	1.1	233
Decane	280.3	253.1	0	1.1	233
Benzene	363.1	342.6	0	1.06	231
Carbon disulfide	445.8	420.6	0	1.06	231
Hexane	238.9	225.1	0	1.06	233
Pentane	220.5	210.0	0	1.05	233
Toluene	354.8	337.2	0.36	1.05	233
Diethyl ether	263.6	250.6	1.2	1.05	233
o-Xylene	356.1	341.8	0.50	1.04	233
Ethyl acetate	355.6	341.8	1.88	1.04	231
Trichloromethane	369.5	361.9	1.1	1.02	233
Methyl acetate	372.4	374.0	1.61	0.99	231
Dichloromethane	407.9	414.2	1.9	0.98	233
Methyl ethyl ketone	341.8	382.8	2.76	0.89	233
Acetone	330.5	394.6	2.88	0.84	231
Dimethylformamide	479.5	582.4	3.82	0.82	231
Dimethyl sulphoxide	520.9	705.4	4.49	0.74	231
Dimethyl sulphoxide	516.7	704.7	4.49	0.733	234
t-Butyl alcohol	338.9	473.8	1.67	0.72	233
Propylene carbonate	543.5	762.7	4.94	0.71	231
Acetonitrile	394.6	582.4	3.84	0.68	231
Butanol	300.0	485.4	1.66	0.62	233
Ethylene glycol	502.1	892.0	2.31	0.56	231
Propanol	287.9	606.7	1.68	0.47	233
Ethanol	292.9	674.9	1.68	0.43	231
Formamide	554.4	1574.9	3.37	0.35	231
Methanol	293.0	860.1	1.66	0.34	234
Methanol	288.3	873.6	1.66	0.33	231
Water	150.6	2302.0	1.84	0.07	231

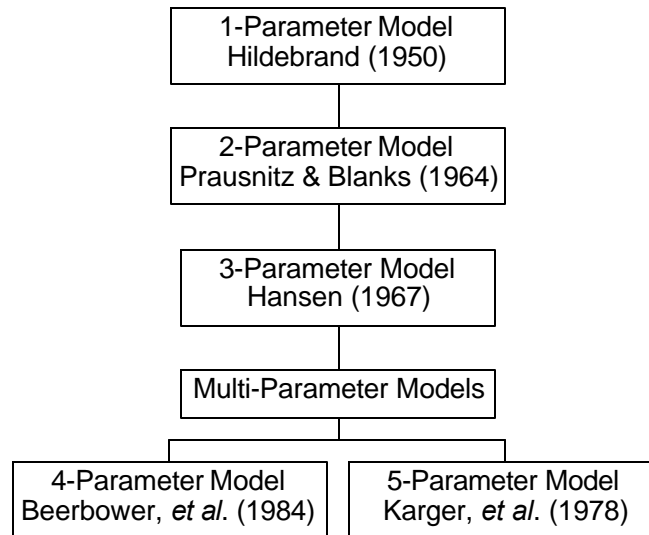


The additional data shown in Table 4-2 further demonstrates that  $n$  is near unity for nonpolar liquids, and also for polar liquids where the dipole moment is less than  $2D$  and where specific interactions (particularly hydrogen bonding) is largely absent. Also, while no direct evaluation of the value of  $n$  has been found in the literature, a comparison of the values in Tables 4-1 and 4-2 strongly suggests that the value of  $n$  for  $\text{CO}_2$ , is expected to be near unity, and as a result, the internal pressure and cohesive energy density are approximately equal. In the remainder of this work, the equivalence of internal pressure and cohesive energy density, at least for the case of  $\text{CO}_2$ , is assumed.

However, in the presence of strong self-association (again, primarily hydrogen bonding),  $n$  is significantly less than unity. The divergence between internal pressure and cohesive energy density in the presence of strong specific interactions can be understood if we examine the physical meaning of  $(\Delta E/V)$  and  $(\partial E/\partial V)_T$ . The cohesive energy density is a measure of the total molecular cohesion, or sum total of the attractive interactions per unit volume when all intermolecular bonds associated with that volume are broken, (i.e., vaporized to an ideal gas). Internal pressure, on the other hand, is a measure of the change in internal energy of 1 mole of solvent as it undergoes a very small isothermal expansion. This small expansion does not necessarily disrupt all the intermolecular interactions associated with 1 mole of solvent. The most important contributions to internal pressure will therefore come from those interactions which vary most rapidly near the equilibrium molecular separation in the solvent (recall  $r_0$  from Figure 3-1). Dispersion, repulsion, and dipole-dipole interactions all vary rapidly with intermolecular separation, see eqns. (3-1), (3-4), and (3-5), and so we might expect the internal pressure to reflect mainly these interactions.<sup>235</sup> This is why, in Tables 4-1 and 4-

2, the values of internal pressure approach those of cohesive energy density for non-polar solvents, and polar liquids where the dipole moment is less than 2 D, where only dispersion and repulsion and weak polar interactions (i.e., no specific interactions) exist. That is, the small volume expansion associated with the internal pressure disrupts the dispersion and repulsion and weak polar interactions as effectively as complete vaporization.

## 4.2 Empirical Models of Solubility Parameters



**Figure 4-1.** Chronological evolution of empirical solubility parameter models.

### 4.2.1 One Parameter Model – (Hildebrand)

The thermodynamic criteria of solubility are based on the Gibbs free energy of mixing,  $\Delta_m G$ . Two substances are mutually soluble if  $\Delta_m G$  is negative. By definition,

$$\Delta_m G = \Delta_m H - T\Delta_m S \quad (4-19)$$

where  $\Delta_m H$  and  $\Delta_m S$  are the enthalpy and entropy of mixing, respectively; and  $T$  is the temperature. As the entropy change of a mixing process,  $\Delta_m S$ , is positive,  $\Delta_m H$  must be negative or slightly positive to have  $\Delta_m G \leq 0$ . Therefore, the miscibility of two compounds depends on the magnitude of  $\Delta_m H$ .

As early as 1916 Hildebrand tried to correlate solubility with the cohesive properties of solvents. In 1949 he proposed the Scatchard-Hildebrand equation for the calculation of the enthalpy of mixing of two liquids.<sup>236</sup>

$$\frac{\Delta_m H}{V} = \left[ \left( \frac{E_1}{V_1} \right)^{1/2} - \left( \frac{E_2}{V_2} \right)^{1/2} \right]^2 \phi_1 \phi_2 \quad (4-20)$$

where  $V$  is the total molar volume of the mixture,  $E_i$  is the molar potential energy or energy of attraction of species 1 and 2 respectively,  $V_1$ ,  $V_2$  are the molar volumes of species 1 and 2, respectively, and  $\phi_1$ ,  $\phi_2$  are the volume fraction of species 1 and 2, respectively.

The energy of attraction,  $E$ , divided by the condensed molar volume was termed by Hildebrand the cohesive energy density, eqn. (4-18), and is the basis of the original definition by Hildebrand and Scott of what is now generally called the *Hildebrand solubility parameter*,  $\mathbf{d}$ . In this definition, Hildebrand equates the energy of attraction  $E$ , with the energy of isothermal vaporization to the gas at zero pressure (i.e. infinite separation of the molecules),  $\Delta E$ . Accordingly, Hildebrand's solubility parameter, defined as the square root of the cohesive energy density,<sup>237</sup> is expressed as

$$\delta = \left( \frac{\Delta E}{V} \right)^{1/2} \quad (4-21)$$

The Scatchard-Hildebrand equation can then be rewritten as

$$\frac{\Delta_m H}{V} = [\delta_1 - \delta_2]^2 \phi_1 \phi_2 \quad (4-22)$$

Examination of eqn. (4-19) shows that the solubility is maximized when  $\Delta_m H$  is minimized, and from eqn. (4-22) it is seen that that this occurs when the respective solubility parameters are equal or when their difference is small. This is in accordance with the general rule that chemical and structural similarity favors solubility, or “like dissolves like”.

In Hildebrand's development of the solubility parameter approach, the existence of polar interactions and of specific interactions such as hydrogen bonding, were explicitly neglected, in other words, he assumed  $n = 1$ . Therefore, the Hildebrand parameter is limited to nonpolar or weakly polar systems where no specific interactions are expected, as in *regular* solutions. Hildebrand describes the term regular solution as “one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged.”<sup>238</sup> It is also necessary to emphasize that the Hildebrand parameter is, fundamentally, a liquid state property. When gases are considered they are treated as hypothetical “liquid” solutes at atmospheric pressure, while substances that are solids at normal temperatures are treated as supercooled liquids.

#### 4.2.2 Two Parameter Model – (Prausnitz and Blanks)

A shortcoming of the early solubility parameter work of Hildebrand is that the approach was limited to solutions of weakly interacting components, as defined by Hildebrand and Scott, and did not account for association between molecules, such as those which polar and hydrogen bonding interactions would require. An early extension of the solubility parameter approach was to systems containing compounds with permanent dipoles. van Arkel,<sup>239</sup> Small,<sup>240</sup> and Prausnitz and co-workers<sup>241</sup> accounted for polar interactions by dividing the total solubility parameter into two components, defining a nonpolar cohesion parameter ( $\delta_D$ ) and a polar parameter ( $\delta_P$ ). Dividing the energy of vaporization of a polar compound into nonpolar and polar parts leads to the following definitions,

$$\text{Nonpolar solubility parameter } \delta_D = \left( \frac{\Delta E_{(np)}}{V} \right)^{1/2} \quad (4-23)$$

$$\text{Polar solubility parameter } \delta_P = \left( \frac{\Delta E_{(p)}}{V} \right)^{1/2} \quad (4-24)$$

where  $\Delta E_{(np)}$  and  $\Delta E_{(p)}$  are the nonpolar and the polar contributions to the energy of vaporization, and

$$\Delta E_{(total)} = \Delta E_{(np)} + \Delta E_{(p)} \quad (4-25)$$

The energy of vaporization of a polar compound was then divided into polar and nonpolar contributions using the homomorph method of Brown.<sup>242</sup> The homomorph method will be described in detail in the next chapter, but, in brief, postulates that the homomorph of a polar molecule is a nonpolar molecule having nearly the same size and shape as that of the polar molecule. This concept is relatively easy to apply, as the energy of vaporization of the polar molecule is simply the difference between the experimentally determined total energy of vaporization and the energy of vaporization of the homomorph molecule, at the same reduced temperature. Blanks and Prausnitz<sup>243</sup> published a homomorphic plot of the energy of vaporization for straight chain hydrocarbons. Similarly, Weimer and Prausnitz<sup>244</sup> prepared homomorph plots of the cohesive pressure against molar volume at various reduced temperatures for alkanes, cycloalkanes, and aromatic hydrocarbons. These figures also have been reproduced elsewhere.<sup>245,246</sup>

#### 4.2.3 Three Parameter Model – (Hansen)

In 1967, Hansen<sup>247</sup> proposed a further extension of the Prausnitz and Blanks 2-parameter model by separating the single polar contribution to the total cohesive energy density into two distinct polar and hydrogen bonding contributions. Therefore, the basis of Hansen Solubility Parameters (HSP) is the assumption that the total cohesive energy ( $E$ ) is made up of the additive contributions from nonpolar (dispersion) interactions ( $E_d$ ), polar (dipole-dipole and dipole-induced dipole) interactions ( $E_p$ ), and hydrogen bonding or other specific association interactions (including Lewis acid-base interactions) ( $E_h$ ):

$$E = E_d + E_p + E_h \quad (4-26)$$

Dividing each contribution by the molar volume gives the square of the total solubility parameter as the sum of the squares of the Hansen dispersion ( $\mathbf{d}_d$ ), polar ( $\mathbf{d}_p$ ), and hydrogen bonding ( $\mathbf{d}_h$ ) components.

$$\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V} \quad (4-27)$$

so that

$$\boxed{\mathbf{d}_T^2 = \mathbf{d}_d^2 + \mathbf{d}_p^2 + \mathbf{d}_h^2} \quad (4-28)$$

where

$$\delta_d^2 = \frac{E_d}{V}; \quad \delta_p^2 = \frac{E_p}{V}; \quad \text{and} \quad \delta_h^2 = \frac{E_h}{V} \quad (4-29)$$

Hansen's total solubility parameter,  $\mathbf{d}_T$ , should equal the Hildebrand solubility parameter, eqn. (4-21), although the two quantities may differ for materials with specific interactions when these specific interactions are determined by different methods.<sup>248</sup>

Hansen's development of the HSP methodology is tied to the reasoning that materials having similar HSP have high affinity for each other, and the extent of the similarity in a given situation will determine the extent of the (favorable) interaction. The same cannot be said of the Hildebrand solubility parameter. Ethanol and nitromethane, for example, have similar Hildebrand solubility parameters (26.1 vs. 25.1 MPa<sup>1/2</sup>), but their affinities are quite different. Ethanol is water soluble, while

nitromethane is not.<sup>249</sup> Hansen has applied the HSP approach, with general success, in predicting polymer solubility that could not have been predicted by Hildebrand parameters. In fact, Hansen demonstrated that mixtures of nitroparaffins and alcohols, which by themselves are nonsolvents for a given polymer, are successfully predicted, through addition of their HSP's, to generate a synergistic mixture which will dissolve the polymer, in agreement with experiment.

It has been shown through numerous examples, by various authors, that the 3-parameter approach of Hansen represents a significant improvement in the description of solubility behavior of real fluids. In addition to polymer solubility (swelling) studies, HSP's have been applied to biological materials, barrier properties of polymers, as well as the characterization of surfaces, pigments, fillers, and fibers.<sup>250</sup> Being able to characterize organic and inorganic solids, liquids, and gases with the same 3-parameter parameter model also enables interpretation of situations involving mutual solubility and material compatibility.

#### 4.2.4 Multi-Parameter Models

Other multicomponent solubility parameter approaches have been developed. Beerbower, Martin, and Wu<sup>251</sup> developed a four-component approach and a five-component approach has been used by a variety of researchers.<sup>252,253,254</sup> In the five parameter approach, the total solubility parameter consists of separate terms for dispersion (induced dipole-induced dipole) interactions ( $d_d$ ), orientation (dipole-dipole) interactions ( $d_o$ ), induction (dipole-induced dipole) interactions ( $d_i$ ), Lewis acid



interactions ( $\mathbf{d}_a$ ), and Lewis base interactions ( $\mathbf{d}_b$ ). Hildebrand's total solubility parameter was related to these component parameters by<sup>255</sup>

$$\mathbf{d}^2 = \mathbf{d}_d^2 + \mathbf{d}_o^2 + 2\mathbf{d}_i\mathbf{d}_d + 2\mathbf{d}_a\mathbf{d}_b \quad (4-30)$$

In the four-component approach, the induction interaction is ignored on the grounds that its inclusion did not improve significantly the solubility predictions, so eqn. (4-30) reduces to<sup>256</sup>

$$\mathbf{d}^2 = \mathbf{d}_d^2 + \mathbf{d}_o^2 + 2\mathbf{d}_a\mathbf{d}_b \quad (4-31)$$

Identifying  $\mathbf{d}_o$  with  $\mathbf{d}_p$  and  $\mathbf{d}_h^2$  with  $2\mathbf{d}_a\mathbf{d}_b$  reduces the 4- parameter model to the 3- parameter (Hansen) model, eqn. (4-28).

Table 4-3 is a comparison of the parameter values obtained with the various solubility parameter models.

**Table 4-3.** Solubility parameter values – empirical models.<sup>257</sup>

Compound	One-Parameter Hildebrand	Two-Parameter	Three-Parameter Hansen	Four-Parameter	Five-Parameter
Chloroform, $\text{CHCl}_3$	$\delta = 19.0$	$\delta_\lambda = 14.9$	$\delta_d = 17.8$	$\delta_d = 17.8$	$\delta_d = 16.6$
		$\delta_\tau = 10.0$	$\delta_p = 3.1$	$\delta_o = 3.1$	$\delta_o = 6.1$
		$\delta_T = 17.9$	$\delta_h = 5.7$	$\delta_a = 6.1$	$\delta_i = 1.0$
			$\delta_T = 18.9$	$\delta_b = 2.7$	$\delta_a = 13.3$
				$\delta_T = 18.9$	$\delta_b = 1.0$
					$\delta_T = 19.3$
Chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$	$\delta = 19.4$	$\delta_\lambda = 18.9$	$\delta_d = 19.0$	$\delta_d = 19.0$	$\delta_d = 18.8$
		$\delta_\tau = 6.0$	$\delta_p = 4.3$	$\delta_o = 4.3$	$\delta_o = 3.9$
		$\delta_T = 19.8$	$\delta_h = 2.0$	$\delta_a = 2.0$	$\delta_i = 0.6$
			$\delta_T = 19.6$	$\delta_b = 1.0$	$\delta_a = -$
				$\delta_T = 19.6$	$\delta_b = 2.1$
					$\delta_T = 19.9$
Dimethyl-formamide $\text{C}_3\text{H}_7\text{NO}$	$\delta = 24.8$	$\delta_\lambda = 17.0$	$\delta_d = 17.4$	$\delta_d = 17.4$	$\delta_d = 16.2$
		$\delta_\tau = 16.5$	$\delta_p = 13.7$	$\delta_o = 13.7$	$\delta_o = 12.7$
		$\delta_T = 23.7$	$\delta_h = 11.3$	$\delta_a = 7.0$	$\delta_i = 4.9$
			$\delta_T = 24.9$	$\delta_b = 9.0$	$\delta_a = -$
				$\delta_T = 24.8$	$\delta_b = 9.4$
					$\delta_T = 24.1$
Dimethyl-sulfoxide, $\text{C}_2\text{H}_6\text{OS}$	$\delta = 24.5$	$\delta_\lambda = 17.5$	$\delta_d = 18.4$	$\delta_d = 18.4$	$\delta_d = 17.2$
		$\delta_\tau = 19.4$	$\delta_p = 16.4$	$\delta_o = 16.4$	$\delta_o = 12.5$
		$\delta_T = 26.1$	$\delta_h = 10.2$	$\delta_a = 4.5$	$\delta_i = 4.3$
			$\delta_T = 26.7$	$\delta_b = 11.7$	$\delta_a = -$
				$\delta_T = 26.7$	$\delta_b = 10.6$
					$\delta_T = 24.9$
Acetone, $\text{C}_3\text{H}_6\text{O}$	$\delta = 20.2$	$\delta_\lambda = 15.7$	$\delta_d = 15.5$	$\delta_d = 15.5$	$\delta_d = 13.9$
		$\delta_\tau = 12.6$	$\delta_p = 10.4$	$\delta_o = 10.4$	$\delta_o = 10.4$
		$\delta_T = 20.1$	$\delta_h = 7.0$	$\delta_a = 4.9$	$\delta_i = 3.1$
			$\delta_T = 20.0$	$\delta_b = 4.9$	$\delta_a = -$
				$\delta_T = 20.0$	$\delta_b = 6.1$
					$\delta_T = 19.6$
1,4-Dioxane, $\text{C}_4\text{H}_8\text{O}_2$	$\delta = 20.5$	$\delta_\lambda = 17.5$	$\delta_d = 19.0$	$\delta_d = 19.0$	$\delta_d = 16.0$
		$\delta_\tau = 9.5$	$\delta_p = 1.8$	$\delta_o = 1.8$	$\delta_o = 10.6$
		$\delta_T = 19.9$	$\delta_h = 7.4$	$\delta_a = 2.1$	$\delta_i = 2.0$
			$\delta_T = 20.5$	$\delta_b = 13.3$	$\delta_a = -$
				$\delta_T = 20.5$	$\delta_b = 9.4$
					$\delta_T = 20.7$

As can be observed from Table 4-3, the three, four, and five parameter approaches generally result in similar values for the total solubility parameter.

However, of all the solubility parameter models, the most widely used has been the 3-parameter approach proposed by Hansen. As a result, there is a large body of tabulated HSP data, both measured and calculated, for a large number of compounds. (The four-parameter approach, should a larger set of data be developed, may become a generally acceptable improvement on the 3-parameter model, as it takes into account the unsymmetrical nature of Lewis acid-base interactions. The five-component approach, which was developed for the optimization of liquid chromatography, has proved too cumbersome for widespread use.<sup>258</sup>) Therefore, because the Hansen 3-parameter model approach provides a reasonable compromise between descriptive accuracy and simplicity, and is well established in the field of solubility characterization, this methodology was chosen for the current work.